BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 606—609 (1968)

Conductance Behavior of Some Hexa-amminecobalt(III) Complexes and Their Ion Association in Aqueous Solutions

Shunzo KATAYAMA and Reita TAMAMUSHI

The Institute of Physical and Chemical Research, Yamato-machi, Saitama

(Received September 7, 1967)

The conductance behavior of some hexa-amminecobalt(III) complexes in dilute aqueous solutions at 25°C was studied in association with the ion-pair formation of hexa-amminecobalt(III) ions. The equivalent conductivities were analyzed according to the Onsager theory, and the thermodynamic formation constants, K, of the ion-pairs, $[Co(NH_3)_6]^{3+}\cdot A^{z_A-}$, were determined. The log K values obtained are 1.4_0 (perchlorate), 1.6_3 (nitrate), 1.6_5 (bromide), 1.3_8 (iodide), and 3.2_5 (oxalate). These values were compared with the formation constants calculated from the spectroscopic data, and discussed in terms of Bjerrum's theory on ion association.

The measurement of electric conductivity of dilute solutions provides a valuable method of studying the outer-sphere ion association of inert complexes. The conductance behavior and the ion association of hexa-amminecobalt(III) chloride,[1,2] sulfate,[2] trimetaphosphate,[3] and tetrametaphosphate[3] in aqueous solutions were studied by Hartley and Donaldson and by Jenkins and Monk. In our previous papers,[4,5] the equivalent conductivities of nitroamminecobalt(III) complexes in dilute aqueous solutions were discussed in terms of the Onsager theory, and the ion-pair formation constants of $[Co(NH_3)_6]^{3+}\cdot Cl^-$ and $[Co(NO_2)(NH_3)_5]^{2+}\cdot Cl^-$ were determined. The present study deals with the conductance behavior and the ion-pair formation of hexa-amminecobalt(III) perchlorate, nitrate, bromide, iodide, and oxalate in dilute aqueous solutions at 25°C.

Experimental

The samples of hexa-amminecobalt(III) chloride, bromide, and iodide were prepared according to the procedure described in the literature.[6] Hexa-amminecobalt(III) perchlorate, nitrate, and oxalate were obtained by adding perchloric acid, nitric acid, and ammonium oxalate, respectively, to the aqueous solutions of hexa-amminecobalt(III) chloride. These samples were carefully purified by three recrystallizations from their aqueous solutions containing a few drops of acetic acid. The purity of the samples was examined by the conventional chemical analysis of the components; the results were in very good agreement with the theoretical values.

The solutions of different concentrations were carefully prepared by using the conductivity water of low specific conductance ($<2\times10^{-7}\Omega^{-1}\,cm^{-1}$) in an atmosphere of purified nitrogen gas. The electric conductivities were measured by the same apparatus as described in the previous papers.[4,5] The resistance readings of the conductivity cell were calibrated by the substitution method using a precision decade resistance box (Dekastat RS-624, Electro Scientific Industries; accuracy, ±0.005%), and their reproducibility was better than 0.1%. All measurements were carried out in a water-thermostat of 25.000±0.005°C.

Results

The hexa-amminecobalt(III) complexes are subjected to the slow decomposition in aqueous solutions; therefore, the conductivities were measured at different times after the preparation of the solution, and the equivalent conductivities at time zero, which were determined by the extrapolation of the measured conductivities against time, were used in the following discussion.[4,5]

The limiting equivalent conductivities, Λ°, of the complexes were determined by Onsager's method of extrapolation[7]: the Λ° of each complex gave consistent values of the limiting ionic equivalent conductivity, λ°, of hexa-amminecobalt(III) ion. The results are summarized in Table 1.

The relation between the equivalent conductivity, Λ, and the concentration, c (equiv./l) was analysed according to the limiting equation of Onsager,[7]

$$\Lambda = \Lambda^\circ - bc^{1/2} \qquad (1)$$

where b is a theoretical constant. Figures 1 and 2 show the plot of Λ against $c^{1/2}$; the broken lines

---

[1] G. S. Hartley and G. W. Donaldson, *Trans. Faraday Soc.*, **33**, 457 (1937).

[2] I. L. Jenkins and C. B. Monk, *J. Chem. Soc.*, **1951**, 68.

[3] C. B. Monk, *ibid.*, **1952**, 1317.

[4] S. Katayama, *Rept. I. P. C. R.*, **42**, 243 (1966).

[5] R. Tamamushi, T. Isono and S. Katayama, This Bulletin, **40**, 334 (1967).

[6] W. C. Fernelius (ed.), "Inorganic Syntheses," II, McGraw-Hill, New York (1946), p. 216.

[7] L. Onsager, *Physik. Z.*, **28**, 277 (1927).

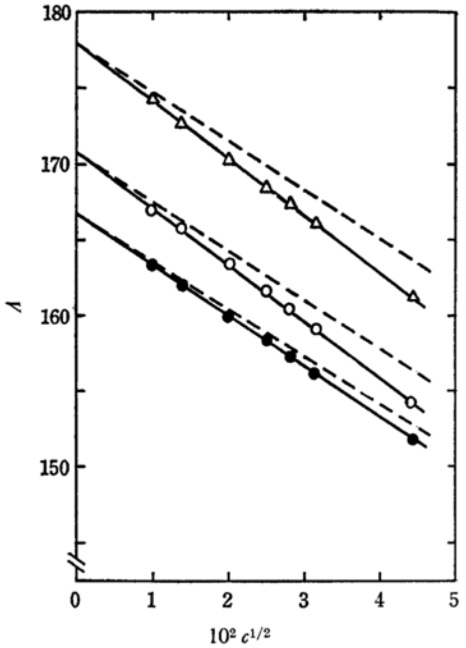

Fig. 1. The Onsager plots of hexa-amminecobalt-(III) perchlorate (-●-), nitrate (-○-), and bromide (-△-) in aqueous solutions at 25°C.

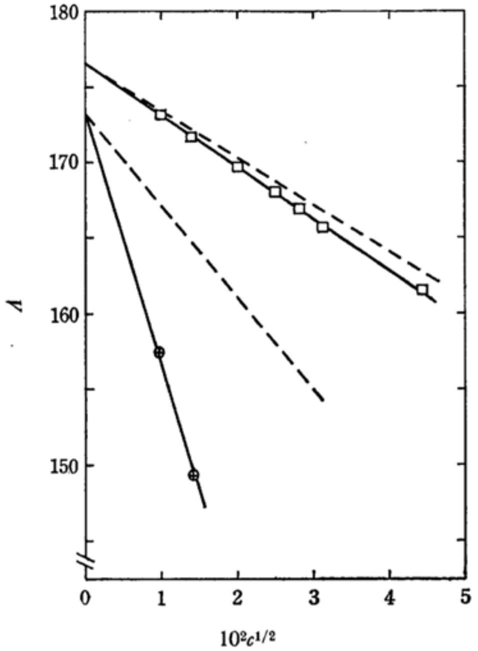

Fig. 2. The Onsagar plots of hexa-amminecobalt-(III) iodide (-□-) and oxalate (-⊕-) in aqueous solutions at 25°C.

represent the theoretical Onsager lines calculated by Eq. (1). The equivalent conductivity of hexa-amminecobalt(III) oxalate gave a large deviation from the theoretical Onsager value even at very low concentrations. A small but significant deviation was also observed with the complexes of $[Co(NH_3)_6]A_3$ type.

Discussion

The deviation of the Λ *vs.* $c^{1/2}$ plot from the theoretical Onsager line in dilute solutions is considered to be due to the outer-sphere association of the complex cation, $[Co(NH_3)_6]^{3+}$, with the anion represented by A^{z_A-},

$$[Co(NH_3)_6]^{3+} + A^{z_A-} \rightleftharpoons [Co(NH_3)_6]^{3+}\cdot A^{z_A-} \quad (2)$$

The degree of dissociation of the possible ion-pairs was determined from the conductivity data according to the successive approximation method of Jenkins and Monk,2) and the concentration formation constants, K_c, of the ion-pairs were calculated at each concentration. In the present calculation, the λ° values of the ion-pairs were estimated from $\lambda^\circ([Co(NH_3)_6]^{3+})$ according to the following equation,

$$\frac{\lambda^\circ(\text{ion-pair})}{\lambda^\circ([Co(NH_3)_6]^{3+})} = \frac{|z|}{3} \quad (3)$$

where z is a net charge of the ion-pair; the equation is obtained from the Stokes' law by neglecting the ion-size effect on the mobility. This estimation of λ°(ion-pair) is rather arbitrary, but it is shown by calculation that a considerable change in λ°(ion-pair) does not affect the derived value of K_c appreciably.8)

By using the modified Debye-Hückel equation suggested by Guggenheim9) for the activity coefficient of an ion, the relation between the thermodynamic and the concentration formation constants, K and K_c, is given by the relation,10)

$$\log K_c + A'\frac{I^{1/2}}{1+I^{1/2}} = \log K + CI \quad (4)$$

where I is the ionic strength, A', a coefficient obtained theoretically from the Debye-Hückel constant and the ionic charges of the ions involved in the ion-pair formation, and C, an arbitrary parameter. The thermodynamic formation constant of each ion-pair was determined by extrapolating the plot of $[\log K_c + A'I^{1/2}/(1 + I^{1/2})]$ against I to infinite dilution (Fig. 3). In Table 2 the present results are compared with the $\log K$ values obtained by Tanaka and his coworkers from the spectroscopic data.11)

---

8) C. B. Monk, "Electrolytic Dissociation," Academic Press, London (1961), pp. 132—133.

9) E. A. Guggenheim, *Phil. Mag.*, **19**, 588 (1935).

10) See for example: G. H. Nancollas, "Interactions in Electrolyte Solutions," Elsevier, Amsterdam (1966), pp. 80—81.

11) N. Tanaka, Y. Kobayashi and M. Kamada, Preprints for the 20th Annual Meeting of the Chemical Society of Japan (1967), p. 30; This Bulletin, **40**, 2839 (1967).

TABLE 1. THE LIMITING EQUIVALENT CONDUCTIVITY, $\Lambda°$, OF HEXA-AMMINECOBALT(III) COMPLEXES AND THE LIMITING IONIC EQUIVALENT CONDUCTIVITY, $\lambda°$, OF HEXA-AMMINECOBALT(III) IONS IN AQUEOUS SOLUTIONS AT 25°C

Complex	$\Lambda°$	$\lambda°([Co(NH_3)_6]^{3+})$
$[Co(NH_3)_6](ClO_4)_3$	166.7	99.3
$[Co(NH_3)_6](NO_3)_3$	170.7	99.3
$[Co(NH_3)_6]Cl_3$	175.8[4,5]	99.5,[4,5] 99.2,[2] 101.9[1]
$[Co(NH_3)_6]Br_3$	177.6	99.5
$[Co(NH_3)_6]I_3$	176.5	99.7
$[Co(NH_3)_6]_2(SO_4)_3 \cdot 5H_2O$	179.2[2]	99.2[2]
$[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$	173.2	99.0

TABLE 2. THERMODYNAMIC FORMATION CONSTANTS OF THE ION-PAIR, $[Co(NH_3)_6]^{3+} \cdot A^{z_A-}$, IN AQUEOUS SOLUTIONS AT 25°C

A^{z_A-}	Thermodynamic formation constant, log K		
	Conductivity	Spectroscopy[11]	Bjerrum's theory
ClO_4^-	1.4_0	—	1.7_8
NO_3^-	1.6_3	—	1.7_9
Cl^-	1.5_5[4,5], 1.49[2]	0.96±0.1	1.8_1[4,5]
Br^-	1.6_5	0.96±0.1	1.8_2
I^-	1.3_8	0.47±0.2	1.8_2
SO_4^{2-}	3.5_6[2]	3.26±0.01	3.1_5
$C_2O_4^{2-}$	3.2_5	—	3.1_0

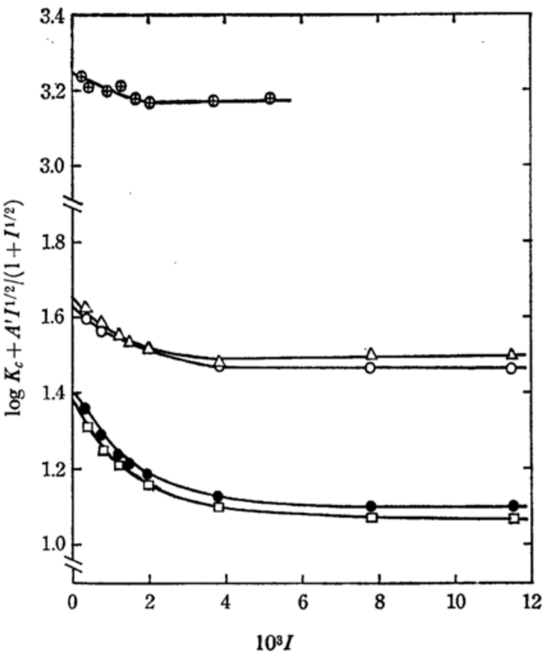

Fig. 3. The determination of thermodynamic formation constants of hexa-amminecobalt(III) perchlorate (-●-), nitrate (-○-), bromide (-△-), iodide (-□-), and oxalate (-⊕-).

If the distance of closest approach of the two ions of an ion-pair is assumed to be equal to the sum of their Stokes radii, the association constant of the ion-pair can be estimated by Bjerrum's theory.[12] The last column of Table 2 presents the log K values calculated theoretically.

In the present analysis of the conductivity data, the deviation of the measured equivalent conductivities from the theoretical Onsager values was entirely attributed to the ion-pair formation of one complex cation with an anion in the solution. Accordingly, the formation constants thus determined may be considered to involve the possible but small contribution from the ion-pairs containing more than one anions. The method of analysis is based upon the assumption that the free ions quantitatively obey the limiting equation of Onsager[7] in dilute solutions, the assumption which, unfortunately, has not been fully examined with higher charge-type electrolytes. Because of this uncertainty involved in the present treatment when applied to the determination of association constants of higher charge-type ions, the results obtained should be subjected to a critical discussion. However, a relatively good agreement of the log K values obtained by the conductivity method with those estimated from Bjerrum's theory (Table 2) suggests that the conductivity method gives reliable information on the ion-pair formation of hexa-amminecobalt(III) ions due to the electrostatic interaction.

A significant difference in the log K values

---

[12] See for example: Ref. 8, pp. 272—275.

determined by the conductivity and spectroscopic methods (Table 2) is supposed to be due to the following reason. The conductometric determination of formation constants is based upon the change in the transport properties of ionic species under electric fields, the properties are not very specific to a particular type of ion interaction. On the other hand, the spectroscopic determination is based upon the change in the charge-transfer spectra; the spectroscopic properties are more specific to the short-range interaction than the transport properties. According to Tanaka and his coworkers, the spectroscopic behavior in the ultraviolet region is expected to give the information on the ion association due to the short-range interactions, and the formation constants determined by this method may be smaller than those obtained from the conductivity data.11)

The perchlorate ion is usually assumed not to form appreciable ion-pairs with most cations in aqueous solutions. In the present study, however, the ion-pair formation of a perchlorate ion with a hexa-amminecobalt(III) ion was observed, the formation constant of which is of the same order of magnitude as that of iodide ion. This effect of the perchlorate ion must be remembered in the study of ion association in solutions containing relatively large amounts of perchlorate ions.